The Semiclassical Model

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Section 1

Electron velocity in the Bloch model

Derivation Part 1

This follows Ashcroft and Mermin Appendix E.

- $H\psi = \left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + U(\mathbf{r})\right)\psi$, where $U(\mathbf{r})$ is a periodic potential
- Of particular interest are the eigensolutions $H\psi = \mathcal{E}\psi$.
- From Bloch's theorem all eigensolutions have the form

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$$

  where $u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$ for all Bravais vectors $\mathbf{R}$

- Apply the Hamiltonian

$$\begin{aligned} H\psi_{n\mathbf{k}} &= \left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + U(\mathbf{r})\right)e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r}) \\ &= e^{i\mathbf{k}\cdot\mathbf{r}}\left(\frac{\hbar^2}{2m}\left(k^2 - 2i\mathbf{k}\cdot\boldsymbol{\nabla} - \boldsymbol{\nabla}^2\right) + U(\mathbf{r})\right)u_{n\mathbf{k}}(\mathbf{r}) \end{aligned}$$

- The eigenvalue equation becomes

$$H_{\mathbf{k}}u_{n\mathbf{k}} \equiv \left(\frac{\hbar^2}{2m}\left(k^2 - 2i\mathbf{k}\cdot\boldsymbol{\nabla} - \boldsymbol{\nabla}^2\right) + U(\mathbf{r})\right)u_{n\mathbf{k}} = \mathcal{E}_{n\mathbf{k}}u_{n\mathbf{k}}$$

Derivation Part 2

Now compute how the eigenvalue changes when **k** changes.

- This is an exercise in quantum perturbation theory.
- Note that

$$H_{\mathbf{k}+\mathbf{q}} = H_{\mathbf{k}} + \frac{\hbar^2}{m}\mathbf{q}\cdot\left(\frac{1}{i}\boldsymbol{\nabla} + \mathbf{k}\right) + \frac{\hbar^2}{2m}q^2$$

- Treat **q** as a perturbation and compute $\mathcal{E}_{\mathbf{k}+\mathbf{q}}$
- Then Ashcroft and Mermin derive first and second derivatives.
- First derivative:

$$\frac{\partial \mathcal{E}_n}{\partial k_j} = \int d^3 r \psi^*_{n\mathbf{k}}(\mathbf{r}) \frac{\hbar^2 \nabla_j}{mi} \psi_{n\mathbf{k}}(\mathbf{r}) = \hbar \frac{\langle p_j \rangle}{m} = \hbar \langle v_j \rangle$$

- So the average single-electron velocity is $\frac{1}{\hbar}\frac{\partial \mathcal{E}_n}{\partial \mathbf{k}}$.

Actually, we care about antisymmetric n-electron wavefunctions. The average n-electron velocity is a sum over individual velocities computed from the $\mathbf{k}_i$ of the n electrons.

Significance of the velocity in the Bloch model

- In Drude or Sommerfeld model, electrons are free between collisions.
- In Bloch model, the eigen-equation includes the ions
  - Eigenstates are stationary so velocity persists forever
- So we need a new model of electron motion

Table 12.1
COMPARISON OF SOMMERFELD AND BLOCH ONE-ELECTRON EQUILIBRIUM LEVELS

	SOMMERFELD	BLOCH
QUANTUM NUMBERS (EXCLUDING SPIN)	$\mathbf{k}$ ($\hbar\mathbf{k}$ is the momentum.)	$\mathbf{k}$, n ($\hbar\mathbf{k}$ is the crystal momentum and n is the band index.)
RANGE OF QUANTUM NUMBERS	$\mathbf{k}$ runs through all of k-space consistent with the Born-von Karman periodic boundary condition.	For each n, $\mathbf{k}$ runs through all wave vectors in a single primitive cell of the reciprocal lattice consistent with the Born-von Karman periodic boundary condition; n runs through an infinite set of discrete values.
ENERGY	$\mathcal{E}(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$.	For a given band index n, $\mathcal{E}_n(\mathbf{k})$ has no simple explicit form. The only general property is periodicity in the reciprocal lattice: $\mathcal{E}_n(\mathbf{k} + \mathbf{K}) = \mathcal{E}_n(\mathbf{k})$.
VELOCITY	The mean velocity of an electron in a level with wave vector $\mathbf{k}$ is: $\mathbf{v} = \frac{\hbar\mathbf{k}}{m} = \frac{1}{\hbar}\frac{\partial\mathcal{E}}{\partial\mathbf{k}}$.	The mean velocity of an electron in a level with band index n and wave vector $\mathbf{k}$ is: $\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar}\frac{\partial\mathcal{E}_n(\mathbf{k})}{\partial\mathbf{k}}$.
WAVE FUNCTION	The wave function of an electron with wave vector $\mathbf{k}$ is: $\psi_{\mathbf{k}}(\mathbf{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{V^{1/2}}$.	The wave function of an electron with band index n and wave vector $\mathbf{k}$ is: $\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$ where the function $u_{n\mathbf{k}}$ has no simple explicit form. The only general property is periodicity in the direct lattice: $u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$.

Section 2

Rules of the semiclassical model

Dependence on band structure

- Band structure is defined by $\mathcal{E}_n(\mathbf{k})$.
- Each electron is specified by $\mathbf{r}, \mathbf{k}$ and n.
- Moreover, electron $(\mathbf{r}, \mathbf{k}, n)$ is identical to electron $(\mathbf{r}, \mathbf{k}+\mathbf{K}, n)$
  - $\mathbf{K}$ is a reciprocal lattice vector so ...
  - Can restrict wave vectors to a primitive cell of reciprocal lattice
- Rules are
  - n is a constant of motion. No interband transitions.
  - $\dot{\mathbf{r}} = \mathbf{v}_n = \frac{1}{\hbar}\frac{\partial \mathcal{E}_n}{\partial \mathbf{k}}$
  - $\hbar\dot{\mathbf{k}} = -e\left[\mathbf{E}(\mathbf{r}, t) + \frac{1}{c}\mathbf{v}_n(k) \times \mathbf{H}(\mathbf{r}, t)\right]$
  - Thermal equilibrium distribution

$$f(\mathcal{E}_n(\mathbf{k}))\frac{d^3k}{4\pi^3} = \frac{d^3k/(4\pi^3)}{e^{\frac{(\mathcal{E}_n(\mathbf{k})-\mu)}{k_B T}} + 1}$$

Comments

- We don't need to look at all bands
  - Ashcroft and Mirman say to look at bands near Fermi level
- $\hbar\mathbf{k}$ is **not** the momentum.
  - It's called the crystal momentum
  - Its rate of change equals the external EM force
  - **p**'s rate of change also includes ionic potential
- The validity of the semiclassical model depends on EM field strength
  - E.g. if the ionic potential is 0, then **E** can change n
  - For non-extreme fields and most metals, validity is good
- Why are equations of motion correct?
  - Ashcroft and Mirman say the justification is difficult
  - In their text, they motivate these but aren't rigorous

Section 3

Some consequences of the semi-classical model

No conduction if bands are filled

- This is covered carefully in Ashcroft and Mirman pp 221-223
- A filled band has the maximum allowed electron k-density.
- A&M show that the semiclassical equations $\implies$ bands stay filled.
- The current density is $\mathbf{j} = \sum_i (-e\mathbf{v}_i)$
  - The i indexes the electrons
- So this sum is approximately

$$\mathbf{j} = (-e) \int_{\mathrm{BZ}} \frac{d^3k}{4\pi^3} \frac{1}{\hbar} \frac{\partial \mathcal{E}}{\partial \mathbf{k}}$$

  where BZ is the first Brillouin zone and $\mathcal{E}$ is the band energy
- $\mathcal{E}$ is periodic over the Brillouin zone
- So by the fundamental theory of calculus, $\mathbf{j} = 0$.

NO CONDUCTION $\implies$ INSULATOR

Transport of holes, due to static **E**, near band upper-edge

- Goal is to find the acceleration, $\mathbf{a} = \frac{d\mathbf{v}}{dt}$ of a charge
- Assume a partially filled band
- Let $\mathbf{k}_0$ be a maximum (upper band edge) of $\mathcal{E}(\mathbf{k})$.
- Recall $\mathbf{v} = \frac{1}{\hbar}\frac{d\mathcal{E}}{d\mathbf{k}}$ then Taylor-expand $\frac{d}{dt}\mathbf{v}$ around $\mathbf{k}_0$.

$$\frac{dv_i}{dt} = \frac{1}{\hbar}\frac{d}{dt}\frac{d\mathcal{E}}{dk_i} = \frac{1}{\hbar}\sum_j \frac{dk_j}{dt}\frac{\partial}{\partial k_j}\left(\frac{\partial \mathcal{E}}{\partial k_i}\right) = \frac{1}{\hbar}\sum_j \frac{dk_j}{dt}\frac{\partial^2 \mathcal{E}}{\partial k_i \partial k_j}$$

- The semiclassical eq'n is $\frac{dk_j}{dt} = -\frac{eE_j}{\hbar}$
- So write $\mathbf{Ma} = -e\mathbf{E}$ where $M_{ij}^{-1} = \frac{1}{\hbar^2}\frac{\partial^2 \mathcal{E}}{\partial k_i \partial k_j}$.
- At a band-maximum, **M** is negative-definite so $\mathbf{Ma} = -e\mathbf{E}$ looks like $F = ma$ for a negative mass and $(-\mathbf{M})\,\mathbf{a} = e\mathbf{E}$ looks like $F = ma$ for a positive charge.
- Define a *hole* to be an unoccupied state (often near top of band).
  - Within any physical system, holes evolve like electrons
  - A hole has a positive charge
  - If electron has negative eff. mass, hole has positive eff. mass
  - Then a hole evolves like $F = ma$ for a positive mass

Section 4

Conductivity

Collisions in the Bloch model

Follows Ashcroft and Mermin Chapter 13.

- Recall: In the Sommerfeld model, the mean-free path (MFP) between collisions, is much larger than the inter-ionic distance.
- Bloch model, for a periodic ionic metal explains that.
  - The Schrodinger equation accounts for all e^--ion interactions
  - So there are no collisions $\implies$ no resistance
    - We'll show that quantitatively later
  - Collisions arise from deviations from periodicity. E.g.
    - impurities
    - thermal vibrations of ions
  - So resistance and MFP have to do with impurities etc.

The relaxation time approximation

Let $g_n(\mathbf{r}, \mathbf{k}, t)\frac{d^3 r d^3 k}{4\pi^3}$ be the number of electrons in the n^{th} band at time t in the semiclassical phase space volume $d^3 r d^3 k$ about the point $\mathbf{r}, \mathbf{k}$.

In equilibrium

$$g_n(\mathbf{r}, \mathbf{k}, t) = f(\mathcal{E}_n(\mathbf{k})) = \frac{1}{e^{\frac{\mathcal{E}_n(\mathbf{k})-\mu}{k_B T}} + 1}$$

where We assume for now that μ, T are $\mathbf{r}$-independent.[1]

Assumptions of the relaxation time approximation.

- In time dt, the probability of collision $= \frac{dt}{\tau_n(\mathbf{k},\mathbf{r})}$.
  - Simplification[2]: assume $\tau_n(\mathbf{k}, \mathbf{r}) = \tau_n(\mathcal{E}_n(\mathbf{k}))$
- Distribution of electrons emerging from a collision is independent of g_n just before the collision.
- If $g_n(\mathbf{r}, \mathbf{k}, t) = f(\mathcal{E}_n(\mathbf{k}))$ just before the collision, then the collision won't change it.

[1] Ashcroft and Mirman allow position-dependence of T and μ but simplify to constants later.

[2] Ashcroft and Mirman p. 429 make this simplification when computing conductivity

Computing dN just after a collision

$$dN(\mathbf{r},\mathbf{k},t) \equiv \frac{d^3 r d^3 k}{4\pi^3} g_n(\mathbf{r},\mathbf{k},t)$$

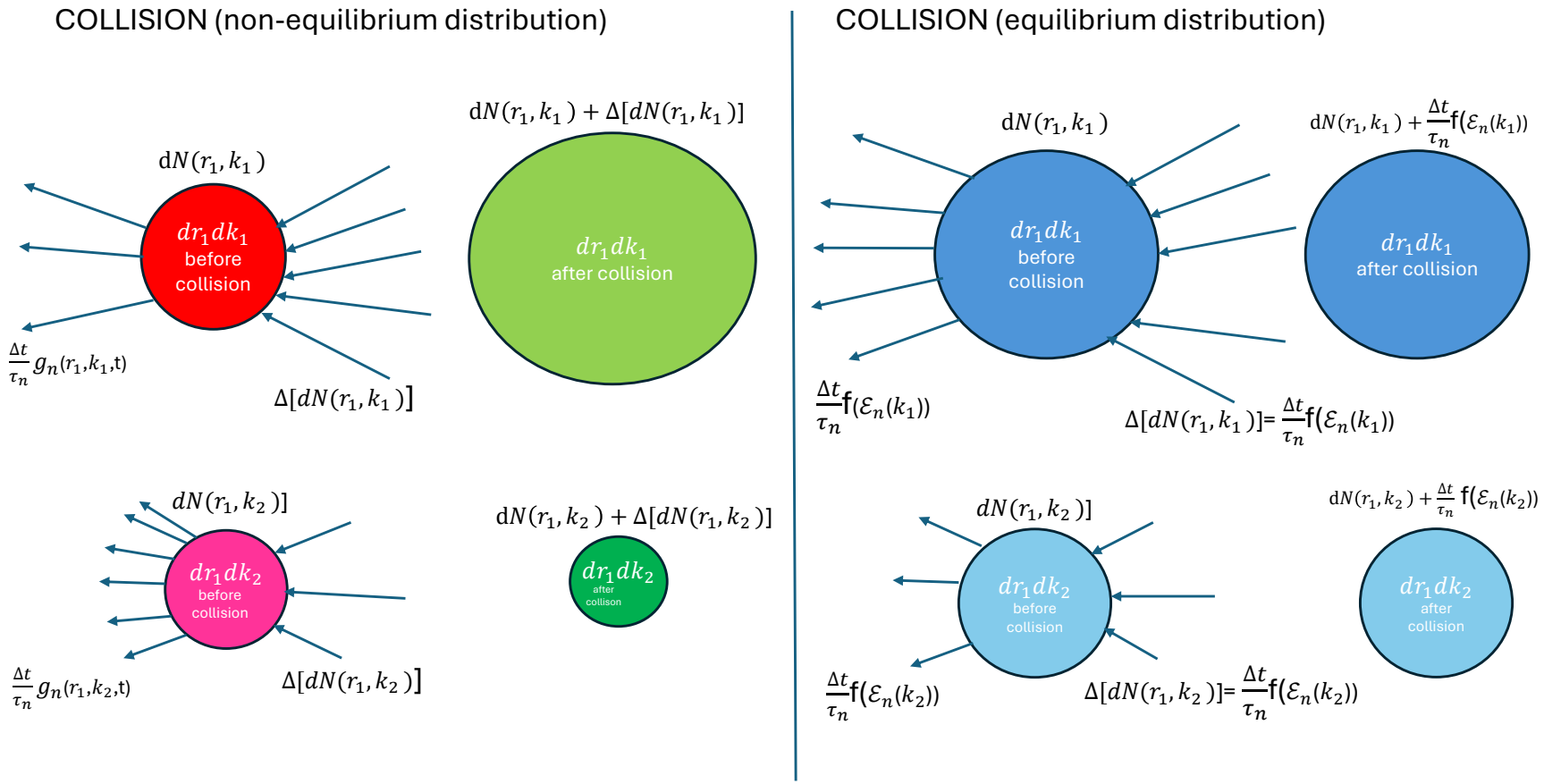


Figure 1: Since $\Delta[dN]$ is distribution-independent, we can replace it on the LHS with $\frac{\Delta t}{\tau_n} f(\mathcal{E}_n(\mathbf{k}))$

Cumulative effect of collisions

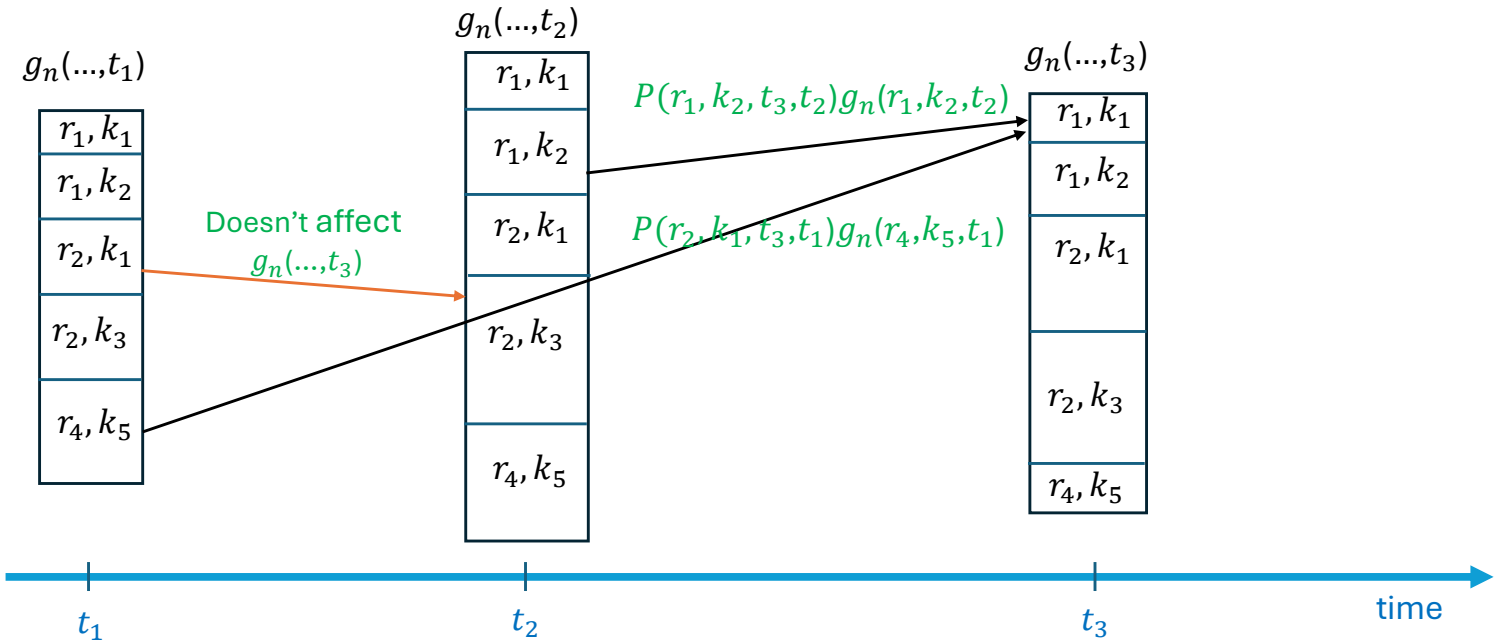


Figure 2: The number of particles with r_1, k_1 at t_3 is the sum of particles arriving from earlier times.

- $g_n(\mathbf{r}_1, \mathbf{k}_1, t_3)$ has a contribution from electrons at time t_2 that followed the semiclassical equations of motion to time t_3.
  - For now, suppress the variables $\mathbf{r}_1.\mathbf{k}_1$.
  - The number of those particles is $\frac{t_3-t_2}{\tau_n} f(\mathcal{E}_n(\mathbf{k}_2))$.
  - Write this as $\frac{t_3-t_2}{\tau_n} f(\mathcal{E}_n(\mathbf{k}(t_2)))$
- $P(\mathbf{r}_1, \mathbf{k}_2, t_3, t_2)$ is the probability that the $(\mathbf{r}_1, \mathbf{k}_2)$ electrons can travel until t_3 without collisions.

Integral form

- Sum up the contributions to $\mathbf{r}_f, \mathbf{k}_f$ at time t from all previous times.

$$g(\mathbf{r}_f, \mathbf{k}_f, t) = \int_{-\infty}^{t} \frac{f(t')}{\tau(t')} P(t, t') dt'$$

  - The index n is suppressed.
  - t'-dependence implicitly comes from the trajectory $\mathbf{r}(t'), \mathbf{k}(t')$ of electrons passing through $\mathbf{r}_f, \mathbf{k}_f$ at time t

- Derive $P(t, t')$
  - Note that

$$\begin{aligned} P(t, t') &= P(t, t' + dt') \times \text{ (prob. of no collision in dt')} \\ &= P(t, t' + dt') \left(1 - \frac{dt'}{\tau(t')}\right) \end{aligned}$$

  - So $\frac{\partial P(t,t')}{\partial t'} = \frac{P(t,t')}{\tau(t')} \implies P(t, t') = \frac{\partial P(t,t')}{\partial t'} \tau(t')$
    - When τ is t'-independent, the solution is $P(t, t') = e^{-\frac{t-t'}{\tau(\mathcal{E}(\mathbf{k}))}}$.

Solving for g in a constant electric field

NB: Ashcroft and Mermin derive equations for a general EM field. We make simplifications that μ and T are constant, the integrand is **r**-independent (p. 249 A&M) and $\mathbf{H} = 0$.

- Substitute for P in our equation for g.[3]

$$\begin{aligned} g(\mathbf{r}_f, \mathbf{k}_f, t) &= \int_{-\infty}^{t} \frac{f(t')}{\tau(t')} \frac{\partial P(t,t')}{\partial t'} \tau(t') dt' = \int_{-\infty}^{t} f(t') \frac{\partial P(t,t')}{\partial t'} dt' \\ &= f(t)P(t,t) - f(-\infty)P(t,-\infty) - \int_{-\infty}^{t} \frac{df(t')}{dt'} P(t,t') dt' \\ &= f(t) - \int_{-\infty}^{t} \frac{df(t')}{dt'} P(t,t') dt' \end{aligned}$$

- f depends on t' as $f\left(\mathcal{E}((\mathbf{k})(t')\right)$.

$$\frac{df}{dt'} = \sum_i \frac{\partial f}{\partial \mathcal{E}} \frac{\partial \mathcal{E}}{\partial k_i} \frac{dk_i}{dt'} = \frac{\partial f}{\partial \mathcal{E}} (\hbar \mathbf{v}) \cdot \dot{\mathbf{k}} = -e \frac{\partial f}{\partial \mathcal{E}} \mathbf{v} \cdot \mathbf{E}$$

- The last equality follows from the semiclassical equation of motion

[3] The last lines use integration by parts: $\int_l^u \frac{df}{dt} g(t) dt = fg(u) - fg(l) - \int_l^u f(t) \frac{\partial g(t)}{\partial t} dt$

The current

- From preceding slides, take P, g and $\frac{df}{dt'}$.
- Also take τ to be t'-independent.

$$g(\mathbf{k}_f) = f(\mathbf{k}_f) + e\int_{-\infty}^{t} e^{-\frac{t-t'}{\tau(\mathcal{E}(\mathbf{k}))}} \frac{\partial f}{\partial \mathcal{E}} \mathbf{v}(\mathbf{k}) \cdot \mathbf{E} dt'$$

$$= f(\mathbf{k}_f) + e\tau(\mathcal{E}(\mathbf{k}_f)) \frac{\partial f}{\partial \mathcal{E}}\Big|_{\mathcal{E}_f} \mathbf{v}(\mathbf{k}_f) \cdot \mathbf{E}$$

- $\mathbf{j} = -e\sum_{\mathbf{k}} \mathbf{v}(\mathbf{k}) g(\mathbf{k}) \xrightarrow[\Delta\mathbf{k}\to 0]{} -e\int \frac{d^3k}{4\pi^3} \mathbf{v}(\mathbf{k}) g(\mathbf{k})$
- Restoring the band index we can write $\mathbf{j}_a = \sum_n \left(\sum_b \boldsymbol{\sigma}_{ab}^{(n)} \mathbf{E}_b \right)$ where

$$\boldsymbol{\sigma}_{ab}^{(n)} = -e\int \frac{d^3k}{4\pi^3} \mathbf{v}_a(\mathbf{k}) g(\mathbf{k})$$

$$= -e^2 \int \frac{d^3k}{4\pi^3} \tau(\mathcal{E}_n(\mathbf{k})) \mathbf{v}_n(\mathbf{k})_a \mathbf{v}_n(\mathbf{k})_b \frac{\partial f}{\partial \mathcal{E}}\Big|_{\mathcal{E}=\mathcal{E}_n(\mathbf{k})}$$

  - We've used the identity $\int d^3k f(\mathbf{k}) \mathbf{v}_n(\mathbf{k}) = 0$ (see Appendix)

Evaluation of σ – part 1

- Suppress the band index n and assume all carriers are in one band.
- f at room temperature is approximately f at $T = 0$.

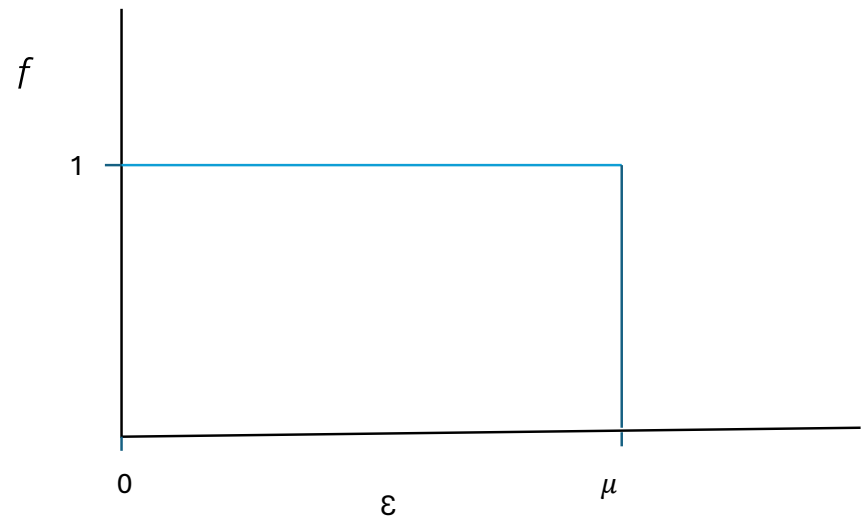


Figure: Fermi-Dirac distribution f as $T \to 0$. $\mu = \mathcal{E}_f$ in the limit.

- $\frac{\partial f}{\partial \mathcal{E}} = -\delta(\mathcal{E} - \mathcal{E}_f)$
  - Caution required during integration over $\mathbf{k}$
  - The delta function is over $\mathcal{E}$ and not k.
  - $\tau(\mathcal{E}(\mathbf{k}))$ can be replaced by $\tau(\mathcal{E}_f)$ and removed from integral.

Evaluation of σ – part 2

- Also notice that $v(\mathbf{k})_a \frac{\partial f}{\partial \mathcal{E}} = \frac{1}{\hbar} \frac{\partial f(\mathcal{E}(\mathbf{k}))}{\partial k_a}$
- Now we have

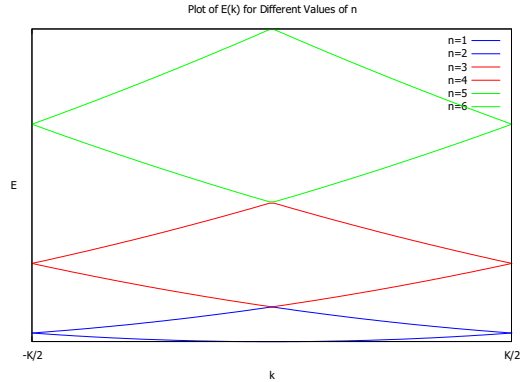
$$\begin{aligned}
\boldsymbol{\sigma}_{ab} &= -e^2 \tau(\mathcal{E}_f) \int \frac{d^3k}{4\pi^3} v(\mathbf{k})_a v(\mathbf{k})_b \frac{\partial f}{\partial \mathcal{E}} \\
&= -e^2 \tau(\mathcal{E}_f) \int \frac{d^3k}{\hbar 4\pi^3} v(\mathbf{k})_a \frac{\partial f(\mathcal{E}(\mathbf{k}))}{\partial k_b} \\
&= e^2 \tau(\mathcal{E}_f) \int \frac{d^3k}{\hbar 4\pi^3} \frac{\partial v(\mathbf{k})_a}{\partial k_b} f(\mathcal{E}(\mathbf{k})) \\
&= e^2 \tau(\mathcal{E}_f) \int_{\text{occupied levels}} \frac{d^3k}{4\pi^3} \frac{\partial^2 \mathcal{E}}{\hbar^2 \partial k_a \partial k_b} \\
&= e^2 \tau(\mathcal{E}_f) \int_{\text{occupied levels}} \frac{d^3k}{4\pi^3} \mathbf{M}^{-1}_{ab}
\end{aligned}$$

Notes on the conductivity tensor

- $\mathbf{M}^{-1}_{ab} = \frac{1}{\hbar}\frac{\partial v_a}{\partial k_b}$,
  - Derivative of a periodic function with period of Brillouin zone
  - So $\int_{\text{Brillouin zone}} d^3k \mathbf{M}^{-1}_{ab} = 0$.
  - So $\int_{\text{occupied levels}} d^3k \mathbf{M}^{-1}_{ab} = \int_{\text{unoccupied levels}} d^3k \left(-\mathbf{M}^{-1}_{ab}\right)$
  - $\implies$ current is due to holes with conductivity $\left(-\mathbf{M}^{-1}_{ab}\right)$.
- Recover the Drude model by setting $\mathbf{M}^{-1}_{ab} = \frac{1}{m^*}\delta_{ab}$
  - Then $\sigma_{ab} = \frac{ne^2\tau}{m^*}\delta_{ab}$
  - Problem: $\int_{\text{Brillouin zone}} d^3k \mathbf{M}^{-1}_{ab} = \int_{\text{Brillouin zone}} d^3k \frac{ne^2\tau}{m^*}\delta_{ab} \neq 0$
  - Note, for the free electron Bloch model, we had $\mathcal{E}(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$.
    - $\mathbf{M}^{-1}_{ab} = \frac{1}{\hbar^2}\frac{\partial^2}{\partial k_a \partial k_b}\frac{\hbar^2 k^2}{2m} = \frac{1}{m}\delta_{ab}$

Resolving the Drude model issue

- Recall the Bloch model for the 1D free electron gas.



$$\psi^c_{nk}(x) = e^{ikx} u^c_{nk}(x) \text{ where } (2\pi)^{\frac{1}{2}}\ u^c_{nk}(x) = e^{i\left(\text{sgn}(k)(-1)^{n-1}\left[\frac{n}{2}\right]K\right)x}$$

u^c_{nk} is periodic.

First Brillouin zone

- In Band 1, $\mathcal{E} = \frac{k^2}{2m}$. Assume full occupation. $v = \frac{1}{\hbar}\frac{\partial \mathcal{E}}{\partial k} = \hbar\frac{k}{m}$
- We had[4]
  $\sigma = e^2\tau(\mathcal{E}_f)\int_{-K/2}^{K/2}\frac{dk}{\hbar\pi}\frac{\partial v(k)}{\partial k} = \lim_{\epsilon\to 0}\frac{e^2\tau}{\hbar}\left(v(K/2+\epsilon) - v(-K/2-\epsilon)\right)$
- So $\sigma = \frac{n}{K}\frac{e^2\tau}{m}\left(K/2 - (-K/2)\right) = \frac{ne^2\tau}{m}$
- If v were periodic, $v(K/2+\epsilon) = v(-K/2+\epsilon) \implies$ discontinuous.

[4]Modified for 1D and setting $f(\mathcal{E}(k)) = 1$ for full occupation

Appendix– Part 1 of proof that $\int d^3k f(\mathbf{k})\mathbf{v}_n(\mathbf{k}) = 0$

First show that $\mathcal{E}_n(\mathbf{k}) = \mathcal{E}_n(\text{-}\mathbf{k})$.

- Recall that

$$H_{\mathbf{k}} = \left(\frac{\hbar^2}{2m} \left(k^2 - 2i\mathbf{k} \cdot \boldsymbol{\nabla} - \boldsymbol{\nabla}^2 \right) + U(\mathbf{r}) \right)$$

and that the eigenvalue equation is

$$\left(\frac{\hbar^2}{2m} \left(k^2 - 2i\mathbf{k} \cdot \boldsymbol{\nabla} - \boldsymbol{\nabla}^2 \right) + U(\mathbf{r}) \right) u_{n\mathbf{k}} = \mathcal{E}_n(\mathbf{k}) u_{n\mathbf{k}}$$

- Conjugate the eigenvalue equation

$$\left(\frac{\hbar^2}{2m} \left(k^2 + 2i\mathbf{k} \cdot \boldsymbol{\nabla} - \boldsymbol{\nabla}^2 \right) + U(\mathbf{r}) \right) u^*_{n\mathbf{k}} = \mathcal{E}_n(\mathbf{k}) u^*_{n\mathbf{k}}$$

- We see that this is $H_{-\mathbf{k}} u^*_{n\mathbf{k}} = \mathcal{E}_n(\mathbf{k}) u^*_{n\mathbf{k}}$.
- Thus $u^*_{n\mathbf{k}}$ is an eigenfunction of $H_{-\mathbf{k}}$ with eigenvalue $\mathcal{E}_n(\mathbf{k})$.
- So $\mathcal{E}_n(-\mathbf{k}) = \mathcal{E}_n(\mathbf{k})$.

Appendix– Part 2 of proof that $\int d^3k f(\mathbf{k})\mathbf{v}_n(\mathbf{k}) = 0$

- The equilibrium function is a function of $\mathcal{E}_n(\mathbf{k}) = \mathcal{E}_n(\text{-}\mathbf{k})$
- So $f(\mathbf{k}) = f(\mathbf{k})$.
- $(\mathbf{v}_n)_i(\mathbf{k}) = \frac{1}{\hbar}\frac{\partial \mathcal{E}_n(\mathbf{k})}{\partial k_i} = -\frac{1}{\hbar}\frac{\partial \mathcal{E}_n(\text{-}\mathbf{k})}{\partial k_i} = -(\mathbf{v}_n)_i(\text{-}\mathbf{k})$
- Finally $\int d^3k f(\mathbf{k})\mathbf{v}_n(\mathbf{k}) = \int d^3k f(\text{-}\mathbf{k})\left(-\mathbf{v}_n(\text{-}\mathbf{k})\right)$
- Then change integration variables in the last term to get

$$\int d^3k f(\mathbf{k})\mathbf{v}_n(\mathbf{k}) = -\int d^3k f(\mathbf{k})\left(\mathbf{v}_n(\mathbf{k})\right)$$

- This completes the proof $\int d^3k f(\mathbf{k})\mathbf{v}_n(\mathbf{k}) = 0$.

Appendix – equilibrium distribution to first order in E

- The function f is the equilibrium distribution for $H_0 - e\mathbf{E}\cdot\mathbf{r}$
- Since $\mathbf{E}$ is directional, $\mathcal{E}(\mathbf{k})$ needn't be spherically symmetrical in $\mathbf{k}$
- However, when $|\mathbf{E}|$ is small, use 1st-order perturbation theory.
  - $\Delta(\mathcal{E}) \propto \int d^3x e^{i\mathbf{k}\cdot\mathbf{x}} e^{-i\mathbf{k}\cdot\mathbf{x}} \mathbf{E}\cdot\mathbf{x}$
  - So $\frac{d}{dk_i}\Delta(\mathcal{E}) = 0$
  - Clean this proof up by putting system in a box
- This proof shows full $\mathbf{k}$-independence of $\Delta(\mathcal{E})$ at 1st-order in $|\mathbf{E}|$.
- So $f(\mathcal{E}(\mathbf{k})) = f_0(\mathcal{E}(\mathbf{k}))$ where f_0 is equilibrium distribution for H_0